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Structural Study of TeO_2-WO_3 Glasses by RDF and Raman Analyses

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Structures of series of TeO_2-WO_3 glasses are studied by X-ray radial distribution function (RDF) and Raman spectroscopic methods. Atomic distances around Te atoms are obtained from the experimental RDF. Structural configuration in nearest neighbor (a variety of polyhedra related to TeO_2 and WO_3 structural components) are obtained from the Raman spectra. From the results of the RDF, Te-O (W-O) interatomic distances are in the range of 0.193–0.194 and Te-Te, 0.364–0.365 nm for $90TeO_2$-$10WO_3$ and $80TeO_2$-$20WO_3$ glasses. The Raman studies for $80TeO_2$-$20WO_3$, $75TeO_2$-$25WO_3$ and $70TeO_2$-$30WO_3$ glasses indicate that there existed TeO_4 trigonal bipyramid, deformed TeO_{3+1} polyhedron and TeO_3 trigonal pyramid associated with TeO_2 component. In relation to WO_3 component, there existed WO_4 tetrahedron and WO_6 octahedron. Structures of TeO_2-WO_3 glasses are basically retained structural conformation found in crystalline paratellurite in spite of that there existed polyhedra of WO_3 component as modifier.

KEY WORDS: Glass Structure/ TeO_2-WO_3 Glasses/ X-ray Distribution Function Analysis/ Raman Spectroscopy

1. INTRODUCTION

Hitherto, the most studies of tellurite glasses have been reported from viewpoints of glass formation[1] as well as optical,[2] dielectric[3] properties and so on. The tellurite glasses are also interesting from structural point of view, because their local structures have possibilities to be formed by variety of coordinates states as represented by TeO_x (x: 4+2, 4+1, 4, 3+3, 3+2, 3+1 and 3) polyhedra found in crystalline states.[4] In tellurite glasses, TeO_2-WO_3 glass should show especially complicate local structures, because of adding to structural configurations such as WO_x (x: 4 and 6) polyhedra. Recently a few structural studies of TeO_2-WO_3 glasses are reported. They are Infra-red (IR) spectroscopic study by Dimitrov *et al.*,[5] Raman spectroscopic one by Gubov *et al.*,[6] neutron diffraction one by Kozhukharov *et al.*[7] and X-ray diffraction one by Nukui *et al.*.[8] Dimitrov *et al.* proposed that part of the TeO_2 was substituted by WO_4 tetrahedra. Gubov *et al.* suggested that two different coordinate states of WO_4 and WO_6 were contributed to build up the glass structure. Kozhukharov *et al.* indicated the influence of WO_3 as the modifier on the Te-O, Te-Te and O-O interatomic distances. Nukui *et al.* indicated that local structure $90TeO_2$-$10WO_3$ was similar to that in paratellurite (α-TeO_2). However, structural conformation by the combination of TeO_x and WO_x polyhedra leads to complicate

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arrangements in the glass structure and has been still remained arguments.

In the present study, we tried to analyze the local structure of TeO_2-WO_3 glasses by combination of Raman spectroscopic and X-ray radial distribution function (RDF) analyses in order to know what kinds of the polyhedra contribute to the local structure and to know atomic arrangement concerned with such the polyhedra.

2. EXPERIMENTAL

The compositions and densities of TeO_2-WO_3 glasses, which were quenched from melt after keeping temperature at 800°C for 30 min., are listed in Table 1. The densities were measured by Archimedes method.

Table 1. Composition and density of the glasses.

Composition	TeO_2 (mol%)	WO_3 (mol%)	Density (g/cm^3)
TW1	90	10	5.68
TW2	80	20	5.93
TW3	75	25	6.06
TW4	70	30	6.18

Samples of TW1 and TW2 were ready for X-ray measurement and TW2, TW3 and TW4, for Raman measurement. X-ray diffraction measurement was performed by using a powder diffractometer[9] at the BL-4B station of Photon Factory in National Laboratory for High Energy Physics. Measurements were carried out by monochromatized X-ray with wave length of 0.075 nm. Intensity data were collected by step scanning with every 0.4° from 4° to 140° in 2θ range adopting fixed-time counting for 30 sec. Intensity of incident beam was monitored by the scattering and fluorescent X-rays from Al foil. The collected intensities were normalized with Krogh-Moe and Norman method after correcting absorption factor and Compton scattering.

The Raman spectra of the glasses were taken in the range of 200–1,200 cm^{-1} with a SPEX RAMALOG9 type spectrometer equipped with an argon ionized laser with 514.5 nm.

3. RESULT

3.1 RDF study

Figure 1 shows intensity curves of the $90TeO_2$-$10WO_3$ and $80TeO_2$-$20WO_3$ glasses. Figure 2 shows the RDF, D(r)'s obtained as the Fourier transform of interference function deduced from the observed intensities. Main peaks located below 0.5 nm are found at 0.193–0.194 nm and 0.374–0.375 nm, and several shoulders in the range of 0.4–0.5 nm for two glasses. The interatomic distances of Te-O including a slight W-O ones, and Te-Te (W-W) in the TeO_2-WO_3 glasses together with those of crystalline α-TeO_2 and Li_2TeO_3 are listed in Table 2.

3.2 Raman Study

Raman spectra of the tellurite glasses with composition of 20, 25 and 30mol% WO_3 contents are shown in Figure 3. In the spectra of the glasses, three bands (around 500, 700 and 930 cm^{-1}) and several shoulders (around 350, 800 and 850 cm^{-1}) are found. The bands below 800–900 cm^{-1} should be mainly contributed by TeO_2 component as refering to Sekiya's Raman

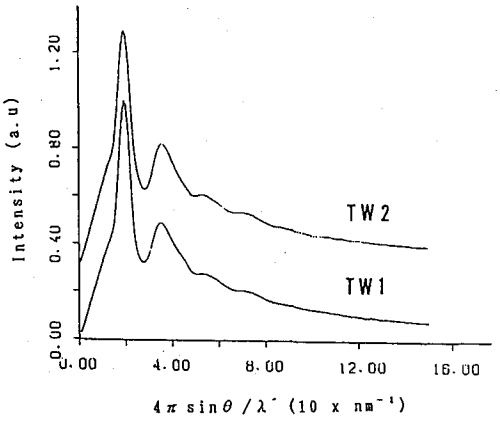

Fig. 1. X-ray diffraction intensities of $90TeO_2$-$10WO_3$ and $80TeO_2$-$20WO_3$ glasses.

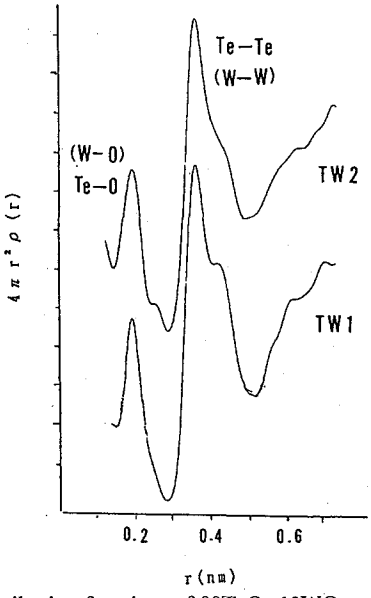

Fig. 2. Radial distribution functions of $90TeO_2$-$10WO_3$ and $80TeO_2$-$20WO_3$ glasses which include mainly local atomic arrangements around Te atoms.

study of a various kind of tellurite glasses.[10] Comparing these spectra with those of the other tellurite glasses with different modifiers such as TeO_2-R_xO_y (ex. R: alkali earth elements and so on),[10] the sharp band beyond the 900 cm^{-1}, relatively large shoulder around 350 cm^{-1} and small one around 850 cm^{-1} are observed additionally. Those correspond to contribution of WO_3 component. Gubov *et al.* proposed that the band at about 930 cm^{-1} was contributed by WO_4 tetrahedron, because B_2WO_4 crystal, which consisted of WO_4 tetrahedra, showed such the band at 930 cm^{-1}. While Daniel *et al.*[11] observed the band in Raman spectra related to tungsten oxide (m and h-WO_3), which consisted of WO_6 octahedra with corner sharing,

Table 2. Interatomic distances of glasses and associated crystals.

	Te-O (nm)	Te-Te (nm)
$90TeO_2$-$10WO_3$	0.194*1	0.364*2
$80TeO_2$-$20WO_3$	0.193*1	0.365*2
α-TeO_2	0.191	0.374
	0.208	
Li_2TeO_3	0.185	0.385
	0.187	
	0.193	

*1 including W-O, *2 including W-W.

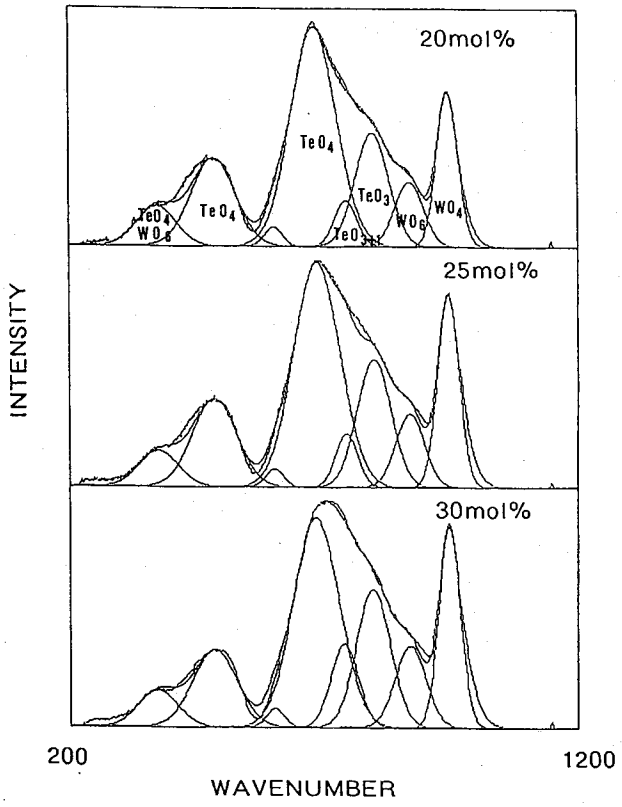

Fig. 3. Raman spectra of $80TeO_2$-$20WO_3$, $75TeO_2$-$25WO_3$ and $70TeO_2$-$30WO_3$ glasses

did not show the band at about 930 cm^{-1}.

The Raman spectra obtained in the present study were deconvoruted by adopting Gaussian functions distributed at the corresponding band positions to those of TeO_4 trigonal bipyramid, deformed TeO_{3+1} polyhedron and TeO_3 trigonal pyramid in TeO_2 component according to Mochida *et al.* and those of WO_4 tetrahedron and WO_6 octahedron in WO_3 component.[6] As the results, the total spectra could be assighned by bands at 780, 650 and 480 cm^{-1} which are

belong to TeO_2 component and by bands at 940, 870 and 380 cm^{-1} for WO_3 component. Furthermore, the band at 780 cm^{-1} is belong to TO_3 polyhedron. That at 720 cm^{-1} is belong to TeO_{3+1} polyhedron, and 650 and 480 cm^{-1}, to TeO_4 polyhedron, respectively. On the other hand, the band at 940 cm^{-1} corresponds to WO_4 tetrahedron, and 870 and 380 cm^{-1}, to WO_6 octahedron, respectively.

4. DISCUSSION

The possible configurations of the polyhedra of TeO_2 component are shown in Figure 4. The Raman analysis indicates the coexistence of a various kinds of primary polyhedra such as TeO_4 trigonal bipyramid (TeO_4 tbp), deformed TeO_{3+1} polyhedron and TeO_3 trigonal pyramid (TeO_3 tp) for TeO_2 component, and WO_4 octahedron and WO_6 octahedron for WO_3 one. While interatomic distance related to the neighbor environment around Te atom such as Te-O and that of Te-Te with slight contribution of W-O and W-W atomic pairs, respectively are obtained by the RDF analysis.

The structures of tellurite glasses are usually explained on the basis of structural units of paratellurite (α-TeO_2) and of the tellurite compounds which have similar compositions to glasses. The structure of α-TeO_2 consists of structure unit which Te atom is surrounded by four oxygen atoms. Two oxygen atoms situated at 0.191 nm in equatorial plane. The other two situated at 0.208 nm in axial plane. While structure of m-WO_3 crystal consists of WO_6 octahedra in which the W atoms are off-center, and form three short (0.18 nm) and three long (0.21 nm) W-O bonds with the surrounding oxygens. The theoretical value of Te-O in TeO_2 glass[6] and the average one in α-TeO_2 are 0.20 nm, respectively. While W-O interatomic distance in the glass is 0.188 nm.[6]

The first peaks found in the RDF for $90TeO_2$-$10WO_3$ and $80TeO_2$-$20WO_3$ are corresponded to Te-O interatomic distances with a small amount of contribution of W-O atomic pairs and located at 0.194 and 0.193 nm, respectively. It is reasonable to show such the values, because of overlapping of Te-O atom pair (0.20 nm) and W-O one with shorter interatomic distance (0.188 nm). The Te-O interatomic distance become short slightly with increasing of WO_3 contents

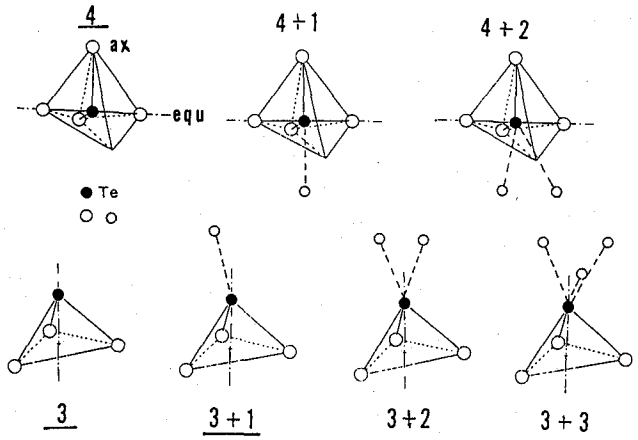

Fig. 4. Schematic illustration of a variety of *possible* polyhedra found in TeO_2 glasses.

from 10 to 20 mol%. This tendency may correspond to configuration change from TeO_4tbp to deformed TeO_{3+1} polyhedra.

The important thing is the difference of the shortest Te-Te distances as well as the first-neighbor Te-O distance. In the results of neutron diffraction by Kuzhukharov *et al.*, they insisted that the peak at 0.38–0.39 nm was strongly diffusive, because this region of atomic arrangement in the glass was affected by the strong deformation of the bonds contributing to the RDF. On the other hand, the results of X-ray diffraction study by Nukui *et al.* and the other tellurite glasses[12] with different elements of compositions indicate that the peak at that region (around 0.37 nm) is extremely large and relatively sharp. There is large difference between the results of neutron and X-ray works. In the neutron experiment, the scattering factor to Te, W and O are almost same to each other. While local structures of TeO_2-WO_3 glasses have retained as a whole, three dimentinal network found in α-TeO_2 from viewpoint of atomic distance of Te-O and Te-Te atom pairs in spite of that the local structure has a variety of polyhedra of TeO_2 and WO_3 components. Therefore, taking into account of the facts described above, the diffuse like shoulder in RDF by the neuron diffraction measurement indicates that "smearing" do not deduce from strong deformation of atomic arrangement in the region (around 0.38 nm) but averaging of the contributions of Te-Te, W-W, the second neighbor Te-O and W-O, and O-O atom pairs, although the tendency of deformation shows to some extent as the results of adding to WO_3 component as modifier or even as networkformer.

Dimitrov *et al.* assumed that the WO_4-tetrahedra a part of TeO_4 groups was replaced by WO_4 tetrahedra, which leads to the formation of Te-O-W-O-Te bonds in the structure, by IR spectroscopic study. With increase in the WO_3 content, WO_4 tetrahedra as well as TeO_{3+1} and TeO_3 polyhedra increase as can be seen in Figure 3. This fact indicate that elongated Te-O bond has possibility to conbine to WO_4 tetrahedron or WO_6 octahedra.

The structural conformation by combination of TeO_x and WO_x polyhedra leads to complicate atomic arrangements through the glass structure. A further study will be performed by partial RDF employing X-ray anomalous scattering in order to make clear the atomic arrangements through the glass structure.

5. CONCLUSION

Structures of series of TeO_2-WO_3 glasses are studied by RDF and Raman spectroscopic methods. Atomic distances around Te atoms are obtained from the RDF. Structural configuration in the nearest neighbor are obtained from the Raman spectra. The Raman studies of series of TeO_2-WO_3 glasses indicate that there existed TeO_4 trigonal bipyramid, deformed TeO_{3+1} polyhedron and TeO_3 trigonal pyramid associated with TeO_2 component. In relation to WO_3 component, there existed WO_4 tetrahedra and WO_6 octahedra. With increase in the WO_3 content, WO_4 tetrahedra as well as TeO_{3+1} and TeO_3 polyhedra increase. Structures of TeO_2-WO_3 glasses are basically retained structural conformation found in crystalline paratellurite in spite of that there existed distinctive polyhedra of WO_3 component.

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